Message

From: Cosler, Doug [DCosler@TechLawInc.com]
Sent: 4/13/2017 7:22:10 PM
To: d'Almeida, Carolyn K. [dAlmeida.Carolyn@epa.gov]; 'Dan Pope' [DPope@css-inc.com]; Brasaemle, Karla [KBrasaemle@TechLawInc.com]; Davis, Eva [Davis.Eva@epa.gov]; Arvind Kutty [AKutty@TechLawInc.com]; Wayne Miller (Miller.Wayne@azdeq.gov) [Miller.Wayne@azdeq.gov]; Eleanor Jennings [ejennings@teci.pro]; steve@uxopro.com
CC: Henning, Loren [Henning.Loren@epa.gov]
Subject: RE: Sampling LNAPL and BIOLNAPL BoxModel

Carolyn,

The physics of this biodegradation problem at ST012 are not necessarily linear due to LNAPL dissolution rates and the issue of possibly running out of electron acceptor (SO4) at some point after active EBR/recirculation/TEA (SO4) addition. Without the active source and with plenty of EA supply, the process is first-order and time achieve a remediation target is inversely proportional to bio rate.

However, with this box model you can see, for example, in the UWBZ (the attached version of the BoxModel) that by reducing their bio utilization rate by 10x (back to measured values) it takes about 10x longer (8.5 yrs vs. 1 yr) following the end of active recirculation to "use up" the 28,000 mg/L sulfate starting concentration. Even if they keep adding SO4, you're right, if the actual bio rate is much less than they used in their model the times to achieve remediation goals will be greatly extended, as we all know.

The active LNAPL dissolution, of course, "complicates things". But, that's why something like his BIOLNAPL box model is good because it constrains the mass balance and allows one to look at "what ifs" and their effects on remediation time frames. Such an analysis tool also allows us to more carefully analyze data from the demonstration field studies.

Doug

From: d'Almeida, Carolyn K. [mailto:dAlmeida.Carolyn@epa.gov]
Sent: Thursday, April 13, 2017 2:50 PM
To: Cosler, Doug <DCosler@TechLawInc.com>; 'Dan Pope' <DPope@css-inc.com>; Brasaemle, Karla <KBrasaemle@TechLawInc.com>; Davis, Eva <Davis.Eva@epa.gov>; Kutty, Arvind <AKutty@TechLawInc.com>; Wayne Miller (Miller.Wayne@azdeq.gov) <Miller.Wayne@azdeq.gov>; Eleanor Jennings <ejennings@teci.pro>; steve@uxopro.com
Cc: Henning, Loren <Henning.Loren@epa.gov>
Subject: RE: Sampling LNAPL and BIOLNAPL BoxModel

Thanks Doug!

I forwarded your previous model comments on to AF already so they have something to look at in the interim.

Do I understand correctly that if Amecs model is assuming a degradation rate 10 times greater than measured, does that bump remedial timeframe estimate from 20 years to 200 years?

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"Because a waste is a terrible thing to mind..."

From: Cosler, Doug [mailto:DCosler@TechLawInc.com]
Sent: Thursday, April 13, 2017 10:53 AM
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Subject: RE: Sampling LNAPL and BIOLNAPL BoxModel

In an attempt to address AMEC's responses below regarding the Groundwater Model and some of the questions that were brought up on recent conference calls, I developed on my own time a biodegradation/LNAPL dissolution model (well-mixed "box model", which is basically what the EBR zone is) that is based on the peer-reviewed BIOLNAPL model developed by the U. of Waterloo (paper attached). The BIONAPL BoxModel is attached as a spreadsheet in which you can easily change input parameters [e.g., initial LNAPL saturation, maximum biodegradation (i.e., utilization) rate, retardation factor, LNAPL dissolution rate, starting SO4 concentration, etc.).

This simplified BIONAPL model is based on the same transport equations in the AMEC Groundwater Model, but the BIONAPL model also includes rate-limited mass transfer from LNAPL to groundwater, which you can see in the BIONAPL model results is very important. The boxmodel computes predicted groundwater concs. (benzene and "other" hydrocarbons), LNAPL saturation, concs. of benzene and "other" in the LNAPL, sulfate concs., total mass in aqueous- and sorbed phases, and LNAPL, etc.

In the attached spreadsheet I have entered values for the UWBZ based on AMEC's modeling report. The LSZ and cobble zone can also be analyzed. I've checked the equations carefully, but this is still a draft model. The box model is set up for a 1.5 year active EBR recirculation/TEA addition (includes groundwater extraction) cycle followed by just EBR for many years.

From my preliminary analyses with the UWBZ it is difficult to see how AMEC will reach the low benzene concentrations they show in Table E-4.15 and remove significant LNAPL (they don't show simulated LNAPL concentration/saturation vs. time in their report) in the required time periods. For example, unless the starting UWBZ LNAPL saturation is much lower than what they assumed and/or they pump a lot more aqueous-phase mass out of the aquifer during active EBR recirculation, these mass balance calculations indicate that they will use up all of the SO4 (28,000 mg/L starting conc.) within a couple of years after the active period ends. Slow LNAPL dissolution (measured at the site by Bo and his colleagues) is also an important factor. They may be counting on the flux of background SO4 into the treatment zone, but this is questionable. Note that they also modeled EBR with a biodegradation (utilization) rate that is 10 times greater than was measured, and they made some confusing statement in the report about how they think the bio half-saturation constant will be much smaller than measured, which would prevent biodegradation from slowing down as suggested by Monod kinetics. Note also, of course, that field conditions will definitely not be well-mixed (e.g., highly-variable permeability), which means that the actual system will not perform as well.

Regardless of these questions, this type of BIOLNAPL model at least gives one a tool to analyze the data obtained during the demonstration period [groundwater concentrations (e.g., benzene, TEX-N and SO4) and LNAPL conc. (per Dan's email today) reductions, field observed bio half-lives, etc.).

Doug

BCT members,

Please see below for responses to comments and questions that came up during our March BCT call. Cathy has reviewed and concurred on the responses. I am sending the message as she currently does not have access to email and Don is traveling.

1. Difference in LNAPL extent characterization in the Cobble Zone between the Draft Final Addendum 2 (Figure B-1) and Figures 1&2 recently distributed before the BCT call.

    a. The presence of LNAPL in the CZ at LSZ23 was interpreted based positive dye tests at depths of 135 and 165 ft bgs (i.e., above and below the CZ). The original LNAPL interpretations assumed positive dye test kits applied to all depths below the test depth until the next dye test result was encountered (very conservative approach). At LSZ23 the PID readings were 2,258 ppmv at 135 ft bgs but decreased to 8.1 ppmv at 145 ft bgs (the approximate top of the CZ). PID values at LSZ23 increased to 1,300 at 160 ft bgs. PID readings indicate that the positive dye tests at 135 ft and 165 ft should not be interpreted that residual LNAPL is continuously present in the CZ. When LNAPL extents were updated follow the EBR drilling, previous boring logs were reviewed and LNAPL interpretations were updated to consider PID readings.

2. Question on the amount of LNAPL removed from inside vs. the TTZ perimeter or outside the TTZ.

    a. It was clarified during the call that the statement on the slide was intended to characterize the entire post SEE period rather than just the period since the January BCT call.
    b. During the period from 13 Jan through 17 March approximately 600 gallons of LNAPL was removed. In the UWBZ approximately 8 gallons came from interior wells out of 109 gallons removed. In the LSZ approximately 237 gallons came from the interior out of 485 gallons removed. (note: we do not account for LSZ16 as an interior well in these estimates based on the lack of another well positioned between LSZ16 and the TTZ perimeter)

3. Request to include baseline microbiological testing.

    a. The addition of baseline qPCR and PLFA will be added for six wells to baseline sampling prior to EBR injections. This will include two wells in each of the three zones (CZ, UWBZ, and LSZ) and will be the same wells proposed for subsequent testing post injections.
    b. SIP analysis is not proposed. The primary purpose of SIP is to demonstrate that carbon atoms from contaminants are incorporated into cell mass and dissolved inorganic carbon to prove degradation is occurring. A positive result is desired during EBR but comparison to a baseline result is irrelevant to the purpose of the test.

4. Comment on calculated kd being excessively low where foc values are low.

    a. Kd values utilized in the EBR model are based on values previously used for the site based on actual field data.
    b. If Kd values were higher as suggested by the comment, it would result in reduced concentration dissolved phase concentrations. By utilizing a higher Kd value in the model, the model would show achieving conditions where the flux of contaminants into dissolved groundwater is addressed by the background flux of TEA sooner than currently predicted by the model (i.e., the current model is sufficiently conservative)
    c. The overall mass at the site is dominated by the LNAPL. The additional sorbed mass associated with a higher kd would not result in a significant change in the overall mass at the site. This is an important consideration; Kd is the equilibrium constant between dissolved and solid phases which both represent a small fraction of the total mass in the presence of LNAPL.

5. Discussion on incorporation of an LNAPL transfer limitation as was used in the SEAM3D code

a. The site-specific LNAPL mass transfer determined during the TEE pilot was based on a continuous active pumping situation without biological enhancement. Although pumping is included in the EBR approach it is primarily for sulfate distribution over a period of several weeks after which pumping ceases. Enhancement of dissolution by biosurfactants is also expected to occur which would have a positive effect on LNAPL mass transfer which is not accounted for in the TEE pilot determination.
b. The MODFLOW-SURFACT code is sufficient as an engineering tool for the purposes of establishing a baseline estimate of EBR performance and duration and evaluating optimization approaches as EBR proceeds. The model will be updated based on actual monitoring results and LNAPL dissolution can be adjusted, if necessary, by adjusting solubility parameters. Other parameters that may affect EBR performance will be adjusted based on monitoring results.

Stuart Pearson, P.E.

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Subject: Sampling LNAPL

Just a note, while everyone is involved with helping Eva finalize the documents, that since AF claims to be depleting the COCs from LNAPL, that it is appropriate then that they consistently sample LNAPL throughout the EBR biotreatment zone just like they are to sample groundwater throughout the EBR treatment zone.